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The absorption of carbon monoxide in COSORB solutions: absorption rate and capacity

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Abstract

Absorption rate experiments and equilibrium experiments were carried out for the COSORB reaction at 300 K. The equilibrium data at 300 K could reasonably well be described with the following relation:

$$K_{eq} = 3.4 \times 10^3 = \frac{[\text{CuAlCl}_4 \cdot \text{tol} \cdot \text{CO}][\text{tol}]}{[\text{CO}][\text{CuAlCl}_4 \cdot \text{tol}_2]}$$

Determination of the kinetics and mechanism of a chemical reaction by means of absorption experiments is possible in the fast reaction regime, where the absorption rate is independent of the mass transfer. In the present study it turned out to be impossible to eliminate the influence of mass transfer, although the experiments were carried out at very low CO partial pressures. This made the determination of the kinetics and mechanism of the forward reaction of the COSORB reaction not possible. The conditions of the present experiments were such that it can be concluded that for absorption equipment design the COSORB reaction can be regarded as instantaneous with respect to mass transfer.

Keywords: Absorption; Kinetics; Mass transfer; Chemical reaction; Vapour liquid equilibrium

1. Introduction

1.1. Use and separation of carbon monoxide

Carbon monoxide is an important basic chemical for the production of many other compounds such as polycarbonate, polyurethane, formic acid, acetic acid and oxo-alcohols. It is produced in large quantities as a mixture of various gases by for example partial oxidation or steam re-forming. Also, carbon monoxide is present in many sidestreams and off gas streams. In order to obtain pure carbon monoxide, it has to be separated from these mixtures which may contain other components, e.g. hydrogen, nitrogen, carbon dioxide, methane and water. For this purpose various (semi)commercial separation processes have been developed, of which the most important are cryogenic distillation, the copper liquor process, pressure swing adsorption (PSA) and the COSORB process [1]. Cryogenic distillation is an expensive separation method. Moreover, the separation of CO in the presence of N₂

is very difficult owing to the similar boiling points. The copper liquor process is among the oldest of the CO separation processes but is nowadays replaced by more efficient techniques. The main problem involved in this gas-liquid process is the stability of the Cu⁺ ion which is used to adsorb CO reversibly; however, it also reacts to give Cu⁰ and Cu²⁺. Another disadvantage is the relatively high pressure needed for the absorption process. Relatively new CO separation processes are the PSA process and the COSORB process which are both based on the capability of Cu⁺ to react reversibly with CO. In the PSA process [2–4], carbon monoxide is adsorbed on alumina or carbon carriers coated with Cu⁺ salts. Although the operation of the PSA process is claimed to be easy, the yield of the process is relatively low [5]. In the COSORB process [6], carbon monoxide is adsorbed and desorbed under mild conditions in a toluene solution which contains a CuAlCl₄ complex. A problem is the high reactivity of CuAlCl₄ complex towards impurities such as H₂O and H₂S which must be removed to the parts per million scale prior to the absorption process.

Besides the above-mentioned processes, various alternative new CO-absorbing or CO-adsorbing systems

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are regularly proposed but not yet industrially applied. Two examples are a selenium-containing amine solution [7] and the so-called HISORB process [8].

1.2. The COSORB process

The COSORB process seems a promising, relatively new technique for the production of high purity CO from gas mixtures; however, basic knowledge and data on the process are scarce in the open literature. A limited amount of information is available on equilibrium data, but in particular the kinetics and mechanism of the reaction have been rarely reported. Both equilibrium data and kinetics are necessary for a proper design of the COSORB absorber and desorber.

McVicker [9] measured the heats of dissociation of CuAlCl_4 and found that, depending on the ratio of $[\text{CuAlCl}_4]$ to $[\text{toluene}]$, the complex is surrounded by either one or two molecules toluene. If toluene is in excess, as observed for the experimentally used COSORB solutions, the complex is embedded by two toluene molecules. Koschel et al. [10] stated that one CuAlCl_4 complex molecule can interact with several CO molecules (up to four); however, it has never been experimentally validated (see [11] for an overview of the equilibrium data). In this survey of the equilibrium experiments a maximum of 1 mol of CO could be dissolved per mole of CuAlCl_4 complex. Therefore the overall reaction can probably be written as



with the equilibrium constant K_{eq} defined as

$$K_{\text{eq}} = \frac{[\text{CuAlCl}_4 \cdot \text{tol} \cdot \text{CO}][\text{tol}]}{[\text{CO}][\text{CuAlCl}_4 \cdot \text{tol}_2]} \quad (2)$$

Usually, in aqueous solutions the solvent concentration is not incorporated in equilibrium expressions because it is relatively high and can be considered as constant. However, in the COSORB process the concentration of toluene changes for high concentrations $\text{CuAlCl}_4 \cdot \text{tol}_2$ and high CO loadings substantially and therefore incorporation in the equilibrium expression is required.

Data on the kinetics of the reaction have been reported by Sato et al. [12] and Gholap and Chaudhari [13]. Although the reaction is very rapid, Sato et al. stated that for their experimental conditions the bulk of the solution was saturated with CO; however, no systematic study was given to verify this assumption. Gholap and Chaudhari [13] measured the absorption rate of CO at industrial conditions and thus high partial pressures. They presented experimentally observed enhancement factors and the corresponding experimental conditions.

In the present study, equilibrium data and adsorption rate experiments are reported for the absorption of CO in 0.14–2.3 M COSORB solutions at 300 K and

at partial pressures up to 0.1 MPa. Also, it will be shown that the results of Gholap and Chaudhari indicate that their kinetic experiments must have been carried out in a regime where the enhancement factor is largely independent of the kinetic rate constant.

2. Theory

2.1. Absorption regime

Generally the absorption rate of CO in a solution in the absence of gas-phase limitation is given by

$$J_{\text{CO}} = k_L E_a (m_{\text{CO}} [\text{CO}]_g - [\text{CO}]_L) \quad (3)$$

If the mass transfer coefficient k_L , the physical solubility m_{CO} of the gas, the liquid composition and the enhancement factor are known, the experimentally observed absorption rates can also be estimated a priori. In order to obtain information about the kinetics from the experimentally observed absorption rates, the absorption must take place in the kinetically or combined mass transfer–kinetically controlled regime [14]. As the COSORB reaction is expected to be fast, the absorption rate experiments must be performed in the combined mass transfer–kinetically controlled regime. In this regime the experiments can best be carried at the so-called pseudo- n th-order conditions, implying no depletion of the liquid phase reactant near the gas–liquid interface. Furthermore, if the experiments are carried out with unloaded solutions, the absorption rate is not affected by the reaction product because the product concentration remains very small.

For a reliable determination of the rate constant in this pseudo- n th-order regime, the following condition must be satisfied:

$$3 < E_a < 0.1 E_{a,\infty} \quad (4)$$

For the general situation of an (n, m) -order reaction of pure CO with the COSORB complex the Hatta number ϕ_a is defined as

$$\phi_a = \frac{\{[2/(n+1)]k_{n,m}(m_{\text{CO}}[\text{CO}]_g)^{n-1}[\text{CuAlCl}_4]_0^m D_{\text{CO}}\}^{1/2}}{k_L} \quad (5)$$

If the experiments are carried out in the regime characterized by Eq. (4), then

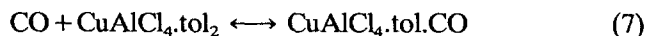
$$E_a = \phi_a \quad (6)$$

which makes it possible to obtain the kinetics for the forward reaction.

2.1.1. Infinite enhancement factor

Because the absorption rate experiments were carried out in a regime with negligible CO loading, the con-

centration of toluene can be considered constant for these experiments. Therefore the absorption rate experiments can be interpreted with a reduced reaction which is given by



in which the reduced equilibrium constant is defined as

$$K_r = \frac{[\text{CuAlCl}_4 \cdot \text{tol} \cdot \text{CO}]}{[\text{CO}][\text{CuAlCl}_4 \cdot \text{tol}_2]} = \frac{K_{\text{eq}}}{[\text{tol}]} \quad (8)$$

For reversible reactions the value of the infinite enhancement factor $E_{a,\infty}$, as used in the determination of the pseudo- n th-order regime (see Eq. (4)) is dependent on the equilibrium constant [15–17]. The infinite enhancement factor for the film model for reaction (7) was originally derived by Olander [15] and is given by

$$E_{a,\infty} = 1 + \frac{D_{\text{CuAlCl}_4 \cdot \text{tol}_2}}{D_{\text{CO}}} \frac{K_r [\text{CuAlCl}_4 \cdot \text{tol}_2]}{D_{\text{CuAlCl}_4 \cdot \text{tol}_2} / D_{\text{CuAlCl}_4 \cdot \text{tol} \cdot \text{CO}} + K_r m_{\text{CO}} [\text{CO}]_g} \quad (9)$$

Because the diffusivity ratio of $\text{CuAlCl}_4 \cdot \text{tol}_2$ to $\text{CuAlCl}_4 \cdot \text{tol} \cdot \text{CO}$ is expected to be about 1, $E_{a,\infty}$ depends on $[\text{CO}]_g$ at high gas concentrations, while at very low gas concentrations the second term in the denominator can be neglected and $E_{a,\infty}$ becomes independent on $[\text{CO}]_g$ (Fig. 1). In order to fulfil Eq. (4), the absorption rate experiments preferably must be carried out with low gas-phase concentration, thereby increasing the value of $E_{a,\infty}$.

If the absorption experiments are carried out in the correct pseudo- n th-order regime the CO absorption rate is independent of the liquid side mass transfer coefficient k_L (combining Eqs. (3), (5) and (6)). This condition must be satisfied for the estimation of the

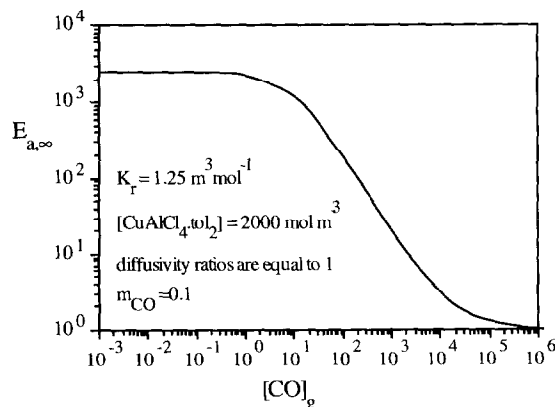


Fig. 1. Infinite enhancement factor for varying gas concentration where the gas concentration is in moles per cubic metre.

Table 1
Solubilities of CO and N₂ in various solvents at 293 K (source, IUPAC)

Solvent	m_{N_2}	m_{CO}	$m_{\text{CO}}/m_{\text{N}_2}$
Acetic acid	0.117	0.169	1.44
Acetone	0.138	0.212	1.54
Toluene	0.120	0.181	1.50
Benzene	0.117	0.177	1.52
Ethanol	0.147	0.201	1.37
Water	0.0167	0.0253	1.52
Chlorobenzene	0.0989	0.148	1.50

mechanism and kinetic constants of the forward reaction [18].

2.2. Estimation of physical parameters

The solubility m_{CO} and mass transfer coefficient k_L of CO in the COSORB solution cannot be measured directly. Nevertheless, these are important parameters in the interpretation of the experiments. Therefore these parameters were estimated by means of an inert “model gas” with great resemblance towards CO. The use of an inert model gas is not new and has already been applied for the “N₂O–CO₂ analogy” [19]. The solubility of CO₂ in reactive aqueous solutions (e.g. aqueous alkanolamine solutions) is estimated by measuring the solubility of the non-reacting N₂O and multiplying it by the ratio of the solubility of CO₂ to that of N₂O in water. Also, information on the mass transfer coefficient k_L of CO₂ in reactive aqueous solutions is obtained by determining the k_L for N₂O in the reactive liquid and thereafter introducing a correction for the difference between the diffusivities of CO₂ and N₂O.

A gas which seems applicable to serve as an inert “model gas” and can be used to replace CO in reactive liquids is N₂, which has a similar molecular weight and size to CO. There is no thorough theoretical background for such an analogy, but because the ratio of the solubilities of both gases in various solvents is almost constant (Table 1), the application of this “N₂–CO analogy” in COSORB solutions seems reasonable.

Moreover, the diffusivities of CO and N₂ estimated with a theoretical model such as that given by Wilke and Chang [20] are almost identical. This was confirmed by the experimentally determined diffusivities of CO and N₂ in toluene at 298 K ($D_{\text{CO}} = 5.60 \times 10^{-9}$ [21]; $D_{\text{N}_2} = 6.12 \times 10^{-9}$ m² s⁻¹ [22]).

3. Experimental set-up and procedure

3.1. Materials

Toluene, CuCl (purity, 97%) and AlCl₃ (purity, 98%) were obtained from Aldrich and used as received. Traces

of water in CO (purity, 99.97%) and N₂ (purity, 99.999%) were removed with silica gel prior to the introduction of the gases in the reactor or preparation vessel.

3.2. Preparation of the COSORB solution

A preparation vessel of about 2 l was filled with toluene and heated to 40 °C. The vessel was flushed with nitrogen to remove air. Next, equimolar amounts of CuCl and AlCl₃ were slowly added to the stirred toluene solution at 40 °C. After introduction of all CuCl and AlCl₃ the vessel was closed and flushed with nitrogen. Subsequently, the solution was stirred for about 4 h to complete the complex forming reaction. The result was an intense black solution with some precipitation on the bottom. In order to remove precipitates the solution was filtered and stored in an air-tight container. This basic solution was used to obtain the desired various CuAlCl₄.tol₂ concentrations by dilution with toluene. Although the CuAlCl₄.tol₂ concentration appeared to be difficult to analyse, the concentration ratios of the experimentally used solutions were accurately known.

3.3. Absorption experiments

A schematic representation of the experimental set-up, which is basically identical with that used by Gholap and Chaudhari [13], is given in Fig. 2. Initially, the absorption rate experiments were carried out by filling an absorption vessel with a known amount of gas and by observing the pressure decrease with time (set-up identical with Fig. 2 except for the constant-pressure regulator which was replaced by a valve). This method is similar to that described by for example Blauwhoff et al. [23]; however, it does not easily allow for low partial gas pressures. Therefore, also another method was used which made it possible to measure the gas absorption rate at relatively low and also constant partial pressures. In this second set-up the gas supply vessel and an absorption vessel were connected via a constant-

pressure regulator. Thus, the pressure in the absorption vessel could be kept constant at a desired (low) partial CO pressure. The pressure decrease in the gas-supply vessel was recorded with a pressure transducer connected to a computer. From this pressure decrease in the gas supply vessel the CO consumption rate in the absorption vessel could be calculated. The pressure in the gas absorption vessel was also continuously recorded to verify whether the CO partial pressure remained constant. The experiments were carried out at various stirring speeds, and hence various mass transfer coefficients, with a virtually flat gas-liquid interface.

For the equilibrium experiments the constant-pressure regulator was replaced by a valve. The gas supply vessel was filled with pure CO, and the valve was opened for a short period. After reaching equilibrium this procedure was repeated several times, until the partial pressure of CO reached a value of about 1 bar.

All equilibrium and absorption rate experiments were carried out with fresh unloaded solutions.

4. Results and discussion

4.1. N₂-CO analogy

In order to estimate the physical solubility and mass transfer coefficient of CO in various COSORB solutions, the solubility and mass transfer coefficient of N₂ were measured. The results are given in Tables 2 and 3. In Table 2 the estimated solubilities for CO according to the CO-N₂ analogy are also presented.

4.2. Equilibrium experiments

The filtrated basic solution had to be analysed to determine the actual CuAlCl₄ concentration. Not only the basic but also the diluted (degree of dilution was known) COSORB solutions were, after destruction of

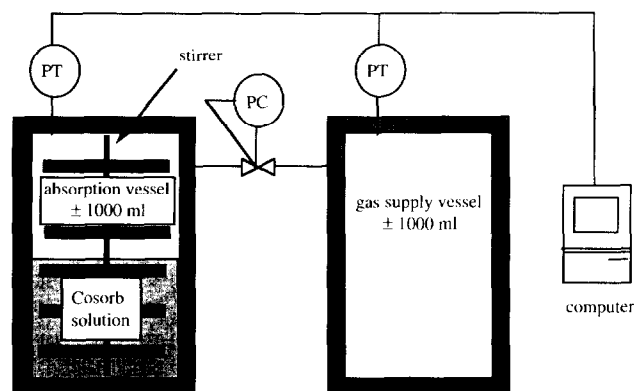


Fig. 2. Schematic representation of experimental set-up.

Table 2

Measured and estimated physical solubilities of N₂ and CO in various COSORB solutions and the mass transfer coefficient of N₂ at identical stirring speeds

CuAlCl ₄ concentration (mol m ⁻³)	N ₂ solubility	Estimated CO solubility	<i>k</i> _{L, N₂} (× 10 ⁻⁵ m s ⁻¹)
0	0.123	0.180 *	6.0
150	0.123	0.180	19.4
480	0.108	0.162	16.7
840	0.093	0.140	13.3
1030	0.086	0.129	10.2
1490	0.061	0.092	6.3
1700	0.059	0.089	5.0
2330	0.053	0.080	—

* Measured.

Table 3

Influence of the stirring speed on the mass transfer coefficient k_L in a 2.33 M COSORB solution at 300 K ($m_{N_2}=0.053$)

Stirring speed (Hz)	k_{L, N_2} ($\times 10^{-5} \text{ m s}^{-1}$)
0.36	1.3
0.43	2.9
0.66	3.5
0.86	5.7

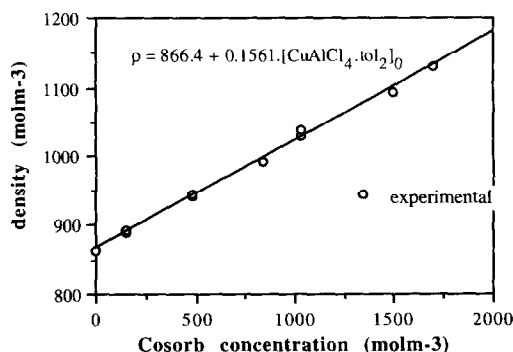


Fig. 3. Density of the COSORB solutions.

the complex, analysed for contents of Al^{3+} , Cu^+ (complexometric) and Cl^- (potentiometric). The analytical results showed a considerable scatter, indicating unreliable data, possibly owing to contact of the samples with air. The expected molar ratios of $Al^{3+}:Cu^+:Cl^- = 1:1:4$ were seldom found, and also the (known) degree of dilution could not be reproduced. Therefore another method was developed to estimate the concentration. At low $CuAlCl_4$ concentrations, toluene is present in excess and the toluene concentration can be considered constant for all CO liquid loadings. The equilibrium expression is for this situation given by Eq. (8) and can be rewritten as

$$[CO]_g = \frac{[CO]_g}{[CO]_{L, tot} - m_{CO}[CO]_g} [CuAlCl_4.tol_2]_0 - \frac{1}{mK_r} \quad (10)$$

In this equation, $[CO]_{L, tot}$ is the total concentration of CO which is absorbed in the COSORB solution and this parameter was experimentally measured. If the term $[CO]_g$ is plotted against the first term of the right-hand side of Eq. (10), the slope of the line gives the initial concentration $[CuAlCl_4.tol_2]_0$. The equilibrium constant was obtained by optimization of K_r , thereby minimizing the difference between the experimental equilibrium results and theoretical results. With this value of K_r , the value K_{eq} could be calculated with Eqs. (8) and (11b) (see Fig. 3 for the density of the COSORB solution) which resulted in $K_{eq} = 3.4 \times 10^3$ for the solution with the lowest concentration.

Now the concentrations of higher concentrated solutions could be estimated, again by minimizing the difference between the experimental equilibrium results and theoretical results (given by Eq. (2)). For this calculation also the concentration of free toluene is required, which depends on the initial $[CuAlCl_4.tol_2]_0$ concentration and the CO loading and can be written as

$$[tol] = [tol]_0 + [CuAlCl_4.tol.CO] \quad (11a)$$

with

$$[toluene]_0 = \frac{(\rho_{COSORB \text{ solution}} - [CuAlCl_4.tol_2]_0 M_{CuAlCl_4.tol_2})}{M_{toluene}} \quad (11b)$$

This toluene concentration can thus be eliminated from Eq. (2), which means that only one parameter (i.e. $[CuAlCl_4.tol_2]_0$) was optimized in the minimization procedure. The experimental densities which are needed in Eq. 11(b) are given in Fig. 3, while the results of the optimization procedure are presented in Table 4. If the equilibrium expression (2) and value are correct, the product of the optimized concentration and the known dilution factor must be identical for all solutions. As can be seen in Table 4, these products agree well, the average being 1650 mol m^{-3} . The optimized concentration of the undiluted basic solution was 1.70 M, which seems reasonable because the basic solution used in the equilibrium experiments was prepared by adding 2 mol of $CuCl$ and $AlCl_3$ per litre of toluene.

The results of the equilibrium experiments are given in Figs. 4 and 5, in which the full curves give the theoretically calculated gas-liquid equilibrium with an equilibrium constant K_{eq} of 3.4×10^3 . From these figures it can be concluded that the results can indeed satisfactorily be described according to the equilibrium ratio (2):

$$K_{eq} = \frac{[CuAlCl_4.tol.CO][tol]}{[CO][CuAlCl_4.tol_2]} \quad (2)$$

Table 4

Estimated concentrations of various COSORB solutions

Optimized concentration	Dilution factor	Dilution factor \times optimized concentration	Concentration of free toluene *
150	10.0	1500	8990
480	3.33	1600	8070
840	2.00	1680	7000
1030	1.54	1580	6590
1490	1.25	1860	5150
1700	1.00	1700	4620
2330	Other solution		2830

* In a CO unloaded COSORB solution based on the measured densities (see Eq. (11b)).

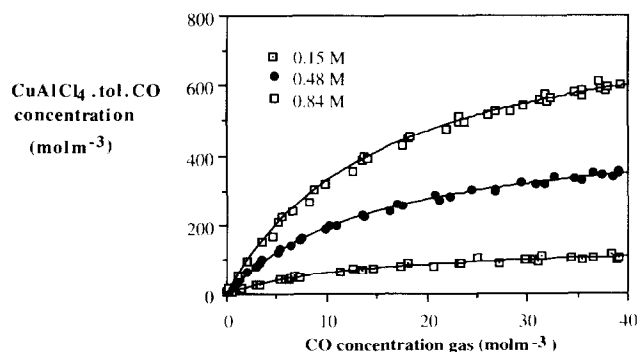


Fig. 4. Equilibrium data at 300 K for solutions with low concentrations.

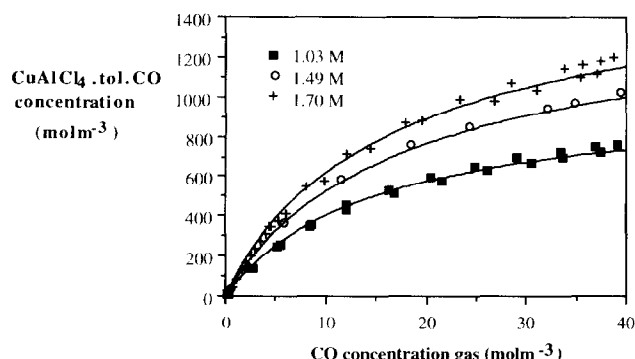
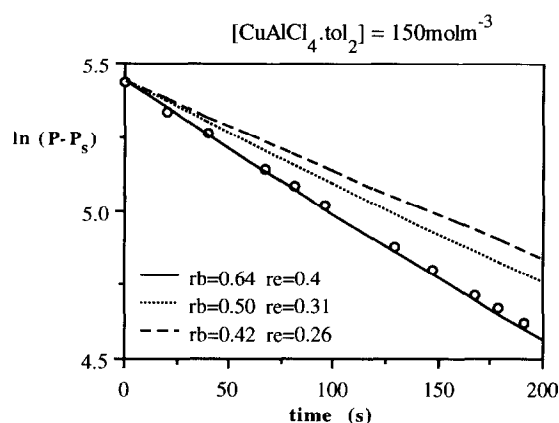


Fig. 5. Equilibrium data at 300 K for solutions with high concentrations.

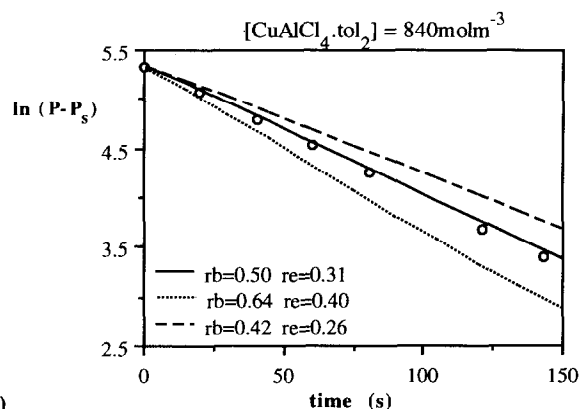
4.3. Absorption rate experiments

A large number of absorption rate experiments with a constant reduction in the (initial) partial pressure were performed. Although the initial partial pressure was considerably decreased, the results all indicated that the experiments were still carried out in or near the instantaneous absorption regime which is described by Eq. (9).

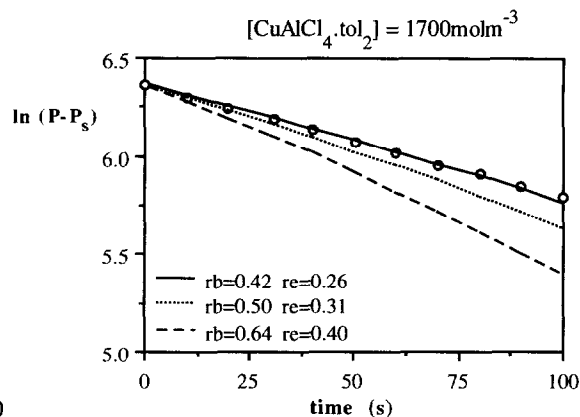
It must be noted that the results obtained in the set-up used initially for the absorption rate experiments with decreasing pressure in the gas absorption vessel (according to the method of Blauwhoff et al. [23], for example) were somewhat misleading. If the absorption rate experiments are carried out in the desired pseudo-first-order regime the plot of $\ln(P - P_s)$ vs. the time should yield a straight line, from which the enhancement factor and thus the kinetic parameters can be determined from Eq. (5). This straight line was also observed in the interpretation of the experiments with the first experimental set-up (Fig. 6) but, nevertheless, the experimentally observed enhancement factors (from $E_a = 16$ to $E_a = 220$) were not in the range of Eq. (4). This paradox was explained by assuming that for these process conditions the absorption in the COSORB solution was totally controlled by mass transfer and that the absorption was carried out in the instantaneous regime. Three examples of the theoretical plot of



(a)



(b)



(c)

Fig. 6. Example of absorption rate experiments obtained with the first experimental set-up (O, experimental results) ($V_{\text{tot}} = 1295$ ml; $A = 5.75 \times 10^{-3}$ m²): (a) 0.15 M, $P_0 = 278$ mbar, $P_s = 48$ mbar, $V_g = 820$ ml, $k_L = 19.4 \times 10^{-5}$ m s⁻¹; (b) 0.84 M, $P_0 = 267$ mbar, $P_s = 60$ mbar, $V_g = 825$ ml, $k_L = 14.4 \times 10^{-5}$ m s⁻¹; (c) 1.70 M, $P_0 = 650$ mbar, $P_s = 71$ mbar, $V_g = 819$ ml, $k_L = 4.8 \times 10^{-5}$ m s⁻¹.

$\ln(P - P_s)$ vs. the time for the instantaneous absorption regime for various concentrated COSORB solutions are given in Fig. 6. In the simulations, r_b ($= D_{\text{CuAlCl}_4.\text{tol}_2}/D_{\text{CO}}$) and the diffusivity ratio r_e/r_b ($= D_{\text{CuAlCl}_4.\text{tol}_2}/D_{\text{CuAlCl}_4.\text{tol.CO}}$) of the two complexes were varied. It was assumed that the diffusivity ratios r_b/r_e of the two complexes were identical for all COSORB concentrations, while r_b could vary with the concentration.

Good agreement between theory and experiment was observed for $r_e/r_b=1.6$, with $r_e=0.40$, $r_e=0.31$ and $r_e=0.26$ for the 0.15 M, 0.84 M and 1.70 M COSORB solutions respectively (see Fig. 6). In order to show the considerable influence of the diffusivity ratio r_b , the various experiments given in Fig. 6 were also simulated with the optimal diffusivity ratios r_b as found for the other concentrations. The results of the simulations indicate that the diffusivity ratio r_b decreases with increase in the concentration of the COSORB solution.

These experiments and simulations clearly show that, if a straight line is observed in presenting $\ln(P-P_s)$ vs. the time, the experiment has not necessarily been performed in the pseudo-first-order regime.

The results of the absorption rate experiments carried out with the second experimental set-up with a constant, relatively low partial pressure of CO also indicated that the absorption occurred in the instantaneous absorption regime. One should note that these experiments were carried out with another high concentrated basic solution. The concentration of this new solution was estimated by equilibrium experiments as described in Section 4.2 and appeared to be 2330 mol m^{-3} with an N_2 solubility of 0.053.

The ratio of the CO absorption rate to the physically dissolved concentration of CO near the gas-liquid interface as a function of the mass transfer coefficient is shown in Fig. 7. Even for these low pressures the absorption rate still depends on the stirring speed, indicating that the experiments were not carried out in the pseudo- n th-order regime (see Eqs. (3), (5) and (6)). Furthermore, the term $J_{\text{CO}}/m_{\text{CO}}[\text{CO}]_g$ seems to be almost independent of the gas concentration, as is expected at low partial pressures in the instantaneous reaction regime (see Eqs. (3) and (9)). In this regime the diffusivity ratio $r_e (=D_{\text{CuAlCl}_4 \cdot \text{tol} \cdot \text{CO}}/D_{\text{CO}})$ can directly be deduced by combining the slope in Fig. 7 (equal to $E_a=395$) and Eq. (9). Thus the diffusivity ratio r_e is found to be 0.14, which seems a reasonable value. This value is smaller than the values found in the first

experimental set-up for the various lower concentrated COSORB solutions. However, these experiments showed that, if the diffusivity ratios r_e/r_b are the same for all COSORB solutions, the diffusivity ratio r_e decreases with increase in concentration. The COSORB solution used in the second experimental set-up had a considerably higher concentration than the solutions used in the first experimental set-up, and therefore the present value for the diffusivity ratio r_e in the second experimental set-up is acceptable.

The results with both set-ups used for the absorption rate experiments indicate that the experiments most probably are carried out in the instantaneous regime, where the absorption rate is totally controlled by mass transfer and determination of the kinetics impossible.

As the industrial COSORB process is operated at moderate pressures ($\pm 10 \text{ bar}$), a CO concentration in the absorber corresponding to a partial pressure of about $\pm 15 \text{ mbar}$ (as applied in these absorption rate experiments), even in the outlet of the reactor, is very unlikely to occur. Therefore the design for a COSORB absorption unit can be based on a reaction instantaneous with respect to mass transfer.

5. Literature data on the kinetics of the COSORB reaction

5.1. Introduction

Literature data on the kinetics of the COSORB reaction were reported by Sato et al. [12] and Gholap and Chaudhari [13]. However, Sato et al. stated that the solution was saturated with CO, although no systematic study was presented to support this opinion. If the present results are taken into account, this assumption seems very unlikely. In the study by Gholap and Chaudhari, much more attention was paid to the interpretation of the absorption rate data; however, the present results and critical evaluation of the data obtained by Gholap and Chaudhari leads to the conclusion that their experiments were, contrary to their opinion, also carried out in an absorption regime which is mainly controlled by mass transfer.

5.2. Experiments of Gholap and Chaudhari

5.2.1. Determination of the enhancement factor

Gholap and Chaudhari determined the experimental enhancement factor which is based on $k_L a$ values and a dimensionless solubility which were measured in pure toluene. However, in Section 4.1 it was shown that both k_L and m_{CO} depend strongly on the $\text{CuAlCl}_4 \cdot \text{tol}_2$ concentration. It is also very likely that the specific contact area a in their experiments also varies with the $\text{CuAlCl}_4 \cdot \text{tol}_2$ concentration. Therefore the calculated

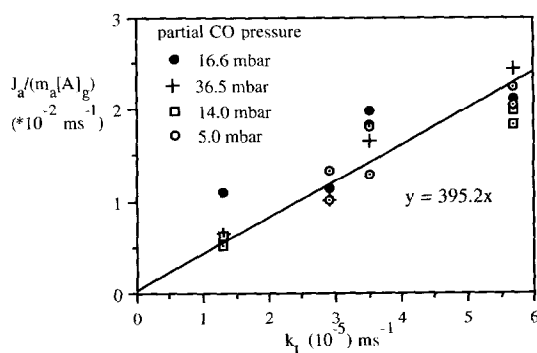


Fig. 7. Results for the absorption rate experiments at low partial CO pressures at 300 K in a COSORB solution of 2330 mol m^{-3} .

values for the enhancement factors obtained for the experiments of Gholap and Chaudhari probably can lead to erroneous results.

5.2.2. Reaction orders

Generally, the rate for a reaction such as the COSORB reaction can be described by

$$R_{\text{CO}} = k_{n,m} (m_{\text{CO}} [\text{CO}]_g)^n [\text{CuAlCl}_4]^m - k_p \times [\text{CuAlCl}_4 \cdot \text{CO}]^p \quad (12)$$

At equilibrium, $R_{\text{CO}} = 0$ and, with the assumption that the kinetic expression still holds at equilibrium, the following result is obtained from Eq. (12):

$$\frac{k_{n,m}}{k_p} = \frac{[\text{CuAlCl}_4 \cdot \text{CO}]^p}{(m_{\text{CO}} [\text{CO}]_g)^n [\text{CuAlCl}_4]^m} \quad (13)$$

Gholap and Chaudhari can describe their equilibrium experiments satisfactorily with a relation similar to the reduced equilibrium expression (8). Only for $n = m = p$ are the two equilibria (8) and (13) coupled via $K_r^n = k_{n,m}/k_p$, which implies that the orders for all components in the kinetic expression have to be identical. However, Gholap and Chaudhari use the parameters n , m and p in the fitting procedure which finally results in $n = p = 1$ and $m = 2$.

5.2.3. Absorption regime and determination of the kinetics

Gholap and Chaudhari have tried to carry out the experiments in the pseudo- n th-order regime, which is characterized by Eq. (4). In this regime the kinetics can be deduced from Eq. (5). The data of Gholap and Chaudhari which were used to determine the kinetics of the reaction are given in Table 5. According to these data the enhancement factor decreases with increasing gas concentration. The enhancement factor for the experiments at, for example, 313 K deviate, for the same $\text{CuAlCl}_4 \cdot \text{tol}_2$ concentration, by a factor of about 2. This means that, if the experiments were carried out in the pseudo- n th-order regime the order in CO had to be smaller than 1 (see Eq. (5)). However, according to Section 5.2.2 the order in CO must be identical with the order in $\text{CuAlCl}_4 \cdot \text{tol}_2$. In their experiments 5-9-10, 15-19-20 and 25-29-30 the enhancement factor at every temperature depends almost linearly on the $\text{CuAlCl}_4 \cdot \text{tol}_2$ concentration. This means that, if the experiments were carried out in the pseudo- n th-order regime (Eq. (6)), the order in $\text{CuAlCl}_4 \cdot \text{tol}_2$ would be about 2. This inequality between the orders n and m is in contradiction with the earlier derived condition of $n = m = p$ (see Section 5.2.2), which indicates that the work of Gholap and Chaudhari was not carried out in the pseudo- n th-order regime given by Eq. (4) but must have been carried out in the regime given by

$$\phi_a > 0.1 E_{a,\infty} \quad (14)$$

Table 5

Data of Gholap and Chaudhari

Run	CuAlCl_4 (mol m ⁻³)	P_{CO} (bar)	E_a , experimental	$E_{a,\infty}$ ^a	$E_{a,\infty}$ ^b
<i>T</i> = 313 K					
1	500	1.8	13.6	13.2	31.5
2	500	2.5	11.9	9.9	23.3
3	500	3.6	9.6	7.6	17.5
4	500	4.3	9.0	6.5	14.7
5	500	7.8	6.9	4.2	8.9
9	750	7.8	10.4	5.7	12.8
10	1000	7.8	13.4	7.3	16.8
<i>T</i> = 333 K					
11	500	1.8	9.3	6.7	15.2
12	500	2.5	8.0	5.8	13.0
13	500	3.6	7.1	5.0	11.0
14	500	4.2	6.1	4.6	9.9
15	500	7.7	5.3	3.3	6.8
16	500	11.1	4.4	2.7	5.3
19	750	7.7	7.6	4.5	9.7
20	1000	7.7	10.2	5.7	12.6
<i>T</i> = 353 K					
21	500	1.8	5.2	4.0	8.4
22	500	2.5	5.0	3.7	7.7
23	500	3.5	4.8	3.4	7.0
24	500	4.1	4.4	3.3	6.6
25	500	7.5	3.8	2.7	5.1
29	750	7.5	6.1	3.5	7.2
30	1000	7.5	8.0	4.3	9.3

^a Calculated with a diffusivity ratio r_b of 0.4.

^b Calculated with a diffusivity ratio r_b of 1.

The influence of the reaction rate on the enhancement factor is very small in this region, and therefore the determination of the kinetics from the experiments difficult and not reliable.

Nevertheless, Gholap and Chaudhari used an approximate analytical solution based on the result of Onda et al. [24] to obtain the kinetics of the reaction in this regime. Versteeg et al. [25] showed that this relation of Onda et al. can give erroneous results for specific reactions and should be used with care. The relation for the enhancement factor for the absorption of CO in an unloaded solution is given by [24,26]

$$E_a = \frac{1 + [(p+1)/(n+1)](r_e/T)}{1 + [(p+1)/(n+1)][(r_e \tanh M_2^{0.5})/TM_2^{0.5}]} \quad (15)$$

with

$$M_2 = M \left(\frac{b_i}{q_b} \right)^m \left(1 + \frac{n+1}{p+1} \frac{T}{r_e} \right) \quad (16)$$

and

$$M = \phi_a^2 \quad (17)$$

$$T = \frac{k_p(m_{\text{CO}}[\text{CO}]_g)^{p-m-n}e_i^{p-1}}{b_i^m k_{n,m}} \quad (18)$$

According to Onda et al. [24] the parameters b_i and e_i can, for an unloaded solution, be evaluated from

$$b_i = q_b - \frac{E_a - 1}{r_b} \quad e_i = \frac{E_a - 1}{r_c} \quad (19)$$

The result of Eq. (15) for reactions instantaneous with respect to mass transfer and $n = m = p = 1$ coincides well with the infinite enhancement factor obtained by Olander [15] for the film theory given by Eq. (9). According to Eq. (9) the infinite enhancement factor decreases at (high) CO concentrations and depends linearly on the $\text{CuAlCl}_4 \cdot \text{tol}_2$ concentration, which is also observed in the data given by Gholap and Chaudhari. This observation indicates that it may even be possible that the experiments of Gholap and Chaudhari were carried out in the diffusion-controlled absorption regime.

This is confirmed if the infinite enhancement factor according to Eq. (9) is calculated for different diffusivity ratios r_e (with $r_e = r_b$). Gholap and Chaudhari calculated the diffusivities of CO and CuAlCl_4 in Eq. (9) with the Wilke and Chang [20] relationship. However, the experimental value for the molecular volume of CuAlCl_4 needed for this calculation is not known. Turner and Amma [27] measured the density of a similar complex of crystalline $\text{CuAlCl}_4 \cdot \text{benzene}$. If the same molecular volume is assumed for the complex in the COSORB solution, it can be derived that $V_{\text{mol}} = 1.66 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$, and the diffusivity ratio r_b is found to be 0.4. Also an optimistic (large) value of 1 for the diffusivity ratio was taken. The results for the infinite enhancement factors obtained with these two diffusivity ratios are also given in Table 5. From this table it can be seen that the experimental enhancement factors lie between the infinite enhancement factors for the two different ratios of the diffusion coefficients. Therefore it seems likely that the experiments were carried out in the diffusion-controlled regime. The determination of the kinetics in this regime is impossible.

5.2.4. Choice of optimization parameters

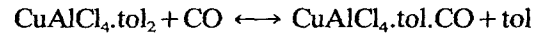
Although Gholap and Chaudhari probably measured the flux in the instantaneous absorption regime they used the approximate expression for the enhancement factor (Eq. (15)) to obtain the kinetics. This involved the fitting of the parameters n , m , p , k_1 , k_{-1} and k_L . However, according to the discussion presented in Section 5.2.3, the parameters m and p do not have to be incorporated in the fitting procedure because they must be taken from the equilibrium experiments which show that $n = m = p$. Also the parameter k_{-1} can be calculated from the theoretical condition $K_r^n = k_1/k_{-1}$

and does not have to be incorporated in the fitting procedure.

Therefore only the parameters n , k_1 and k_L had to be optimized, while Gholap and Chaudhari fitted the parameters n , m , p , k_1 , k_{-1} and k_L . The optimization of the parameters suggested here would have avoided the somewhat strange conclusions that $K_r^n \neq k_1/k_{-1}$ and $n = p \neq m$.

6. Conclusions

Absorption rate experiments and equilibrium experiments were carried out for the COSORB reaction at 300 K. The equilibrium reaction at 300 K could reasonably well be described with the following relation:



with

$$K_{\text{eq}} = \frac{[\text{CuAlCl}_4 \cdot \text{tol} \cdot \text{CO}][\text{tol}]}{[\text{CO}][\text{CuAlCl}_4 \cdot \text{tol}_2]} = 3.4 \times 10^3$$

In order to increase the infinite enhancement factor, the absorption rate experiments were carried out at low CO partial pressures. Nevertheless, the absorption was controlled by mass transfer, which made the determination of the reaction mechanism and rate constants impossible. A critical evaluation of the results of Gholap and Chaudhari [13] also leads to the conclusion that the experiments of these workers were, contrary to their opinion, carried out in an absorption regime dominated by mass transport. For equipment design, the COSORB reaction can be regarded as instantaneous with respect to mass transfer.

Appendix A: Notation

A	contact area between gas and liquid (m^2)
b_i	$[\text{CuAlCl}_4]/m_{\text{CO}}[\text{CO}]_g$ at interface (–)
D	diffusivity ($\text{m}^2 \text{ s}^{-1}$)
E_a	enhancement factor (–)
$E_{a,\infty}$	infinite enhancement factor (–)
e_i	$[\text{CuAlCl}_4 \cdot \text{CO}]/m_{\text{CO}}[\text{CO}]_g$ at interface (–)
J_{CO}	flux of component A ($\text{mol m}^{-2} \text{ s}^{-1}$)
k_L	liquid side mass transfer coefficient (m s^{-1})
$k_{n,m}$	reaction rate constant for reaction of n th order in CO and m th order in CuAlCl_4 ($(\text{mol m}^{-3})^{-n-m+1} \text{ s}^{-1}$)
k_p	reaction rate constant for reaction of p th order in $\text{CuAlCl}_4 \cdot \text{CO}$ ($(\text{mol m}^{-3})^{-n+1} \text{ s}^{-1}$)
K_{eq}	equilibrium constant (–)
K_r	reduced equilibrium constant in Eq. (8) ($\text{m}^3 \text{ mol}^{-1}$)
m_{CO}	partition coefficient of CO (–)
P	pressure (bar)
P_s	vapour pressure of COSORB solution (bar)
q_b	$[\text{CuAlCl}_4 \cdot \text{tol}_2]_0/m_{\text{CO}}[\text{CO}]_g$ (–)

r_b	$D_{\text{CuAlCl}_4, \text{tol}}/D_{\text{CO}}$ diffusivity ratio (–)
r_e	$D_{\text{CuAlCl}_4, \text{CO, tol}}/D_{\text{CO}}$ diffusivity ratio (–)
V_g	gas volume (m^3)
V_{tot}	total volume of absorption vessel (m^3)

Greek letter

ϕ_a	Hatta number
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Subscripts and superscripts

0	initial or bulk condition
g	gas phase
n, m, p	reaction orders for CO, CuAlCl_4 and CuAlCl_4CO respectively

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